ELUCIDATION OF STRUCTURE FROM MOLECULAR FORMULA AND SPECTRAL DATA

<u>Step 1:</u> Find the <u>index of hydrogen deficiency</u>, also known as the number of elements of unsaturation:

$$\text{Elements of unsaturation (e.u.)} = \frac{2 \times C + 2 - H - X + N}{2}$$

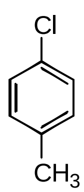
The number of e.u. corresponds to the number of multiple bonds OR rings OR multiple bonds + rings

For example: C_7H_7Cl

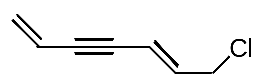
$$\text{e.u.} = (2 \times 7 + 2 - 7 - 1)/2 = 4$$

Thus the molecule may have: 4 double bonds OR 2 double + 1 triple bond OR two triple bonds OR 1 ring + 3 double bonds OR ….

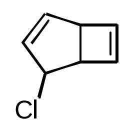
Possible structures (Other exist besides the ones below!!!!):



one ring + three double bonds



two double + one triple bond



two rings + two double bonds

In general: Each e.u. is equivalent to ONE ring or ONE π-bond

<u>Step 2:</u> Use MS data to obtain info about potential functional groups that would not show in the NMR spectrum (i.e. halogens, also info about alcohols, amines). If molecular formula is not given, extract information about molecular weight (i.e. the m/z for the molecular ion). Check fragmentation pattern and compare with NMR signals to get clues on possible sub-structures.

<u>Step 3:</u> Find out the number of signals in the proton NMR. Hopefully (although not necessarily) it corresponds to the number of groups (sets) of equivalent H-atoms.

<u>Step 4:</u> Integration – obtain ratio of non-equivalent H-atoms. Check if the sum matches the actual number of H-atoms (from molecular formula!) or the actual number is a multiple of the simplest ratio. Obtain the correct number of H-atoms for each NMR signal.

<u>Step 5:</u> Chemical shifts – using the chemical shift values, try to extract information about the potential environment for each set of equivalent hydrogens. Use the table of chemical shifts and coupling constants.

<u>Step 6:</u> Splitting pattern – use it to further verify the nature of groups (Learn some common patterns, e.g. ethyl, *i*-propyl, propyl, *p*-substituted benzene ring).

<u>Step 7:</u> If ^{13}C NMR is provided, obtain the number of non-equivalent C-atoms. It can be quite a useful tool for the construction of the molecular skeleton, together with Step 8.

Step 8: If off-resonance ^{13}C NMR is provided, use it to obtain information on the particular pattern of substitution of each C-atom (i.e. CH3, CH2, CH or C). See if your results match previous conclusions from 1H NMR.

Step 9: Connect the sub-structures into a meaningful structural formula. Do not make any gross mistakes, such as pentavalent carbon, etc.

<u>Step 10</u> (It is not actually a step): Cross-check data several times. If any piece of data conflicts the structure that you have proposed, try to think of another structure. Do not settle with a structure just because it fits nicely, say, 60% of the data but obviously contradicts the other 40%. But be flexible somewhat as well: The chemical shift values in the table that I have provided are NOT ALL INCLUSIVE. In some cases actual shifts could be outside the range (but not too far!).